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Title: ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

Abstract:

An etching solution which contains hydrogen fluoride (HF) and exhibits an etching rate ratio: etching rate for a boron-glass film (BSG) or boron-phosphorusglass (BPSG)/etching rate for a thermally oxidized film (THOX) of 10 or more at 25 DEG C.



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(54) ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE

(57) An etching solution which contains hydrogen fluoride (HF) and exhibits an etching rate ratio: etching

rate for a boron-glass film (BSG) or boron-phosphorus-glass (BPSG)/etching rate for a thermally oxidized film (THOX) of 10 or more at 25°C.

Description

TECHNICAL FIELD

[0001] The present invention relates to an etching solution, a method for producing an etched article and an etched article produced by the method, more specifically, an etching solution and a method for producing an etched article for selectively etching a doped oxide film, particularly BSG or BPSG relative to an undoped oxide film, particularly THOX, and an etched article produced by the method.

10 BACKGROUND ART

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[0002] Conventionally, as etchants for silicon wafers and the like have been used buffered hydrofluoric acids comprising HF (50% by weight) and NH₄F (40% by weight) at such a ratio that can achieve a desired etch rate.

[0003] However, the buffered hydrofluoric acids etch not only doped oxide films such as BSG films, BPSG films, phosphosilicate glass (PSG) films, arsenic silicate glass (AsSG) films and the like, but also undoped oxide films such as USG including TEOS (oxide obtained by CVD method using tetraethoxysilane gas) films, THOX and the like. Therefore, the buffered hydrofluoric acids can not selectively etch the doped oxide films.

[0004] An object of the present invention is to provide an etching solution and an etching method for selectively etching oxide films doped with impurities relative to TEOS and THOX.

DISCLOSURE OF INVENTION

[0005] The present invention relates to the items 1-16 listed below.

25 Item 1: An etching solution comprising hydrofluoric acid, wherein an a ratio of etch rate of a boron silicate glass film (BSG) or boron phosphosilicate glass / an etch rate of a thermal oxide film (THOX) at 25°C is 10 or higher.

Item 2: The etching solution according to item 1, wherein a solvent in the etching solution has a relative dielectric constant of 61 or lower.

Item 3: The etching solution according to item 1, the solution containing at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.

Item 4: The etching solution according to item 1, the solution containing (i) water and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 70% by weight or lower.

Item 5: The etching solution according to item 1, wherein the weight ratio of HF: isopropyl alcohol: water is 0.1-50% by weight: 30-99% by weight: 0-70% by weight.

Item 6: The etching solution according to item 1, wherein the weight ratio of HF: acetic acid: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 7: The etching solution according to item 1, wherein the weight ratio of HF: tetrahydrofuran: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 8: The etching solution according to item 1, wherein the weight ratio of HF: acetone: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 9: The etching solution according to item 1, wherein the weight ratio of HF: methanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 10: The etching solution according to item 1, wherein the weight ratio of HF: ethanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 11: The etching solution according to item 1, the solution comprising an inorganic acid.

Item: 12 The etching solution according to item 11, wherein the inorganic acid has a pKa value at 25°C of 2 or lower. Item 13: The etching solution according to item 11, wherein the weight ratio of HF: HCI: water is 0.01-50% by weight: 1-36% by weight: 0-99% by weight.

Item 14: The etching solution according to item 11, wherein the weight ratio of HF: HNO₃: water is 0.01-50% by weight: 1-70% by weight: 0-99% by weight.

Item 15: A method for producing an etched article by etching an article to be etched with the etching solution as defined in any of items 1-14.

Item 16: An etched article which is obtainable by the method of item 15.

[0006] According to the etching solution of the invention, the ratio of BSG etch rate / THOX etch rate and/or the ratio of BPSG etch rate / THOX etch rate at 25°C is/are 10 or higher, preferably 20 or higher, more preferably 50 or higher, particularly 100 or higher.

[0007] In case of using TEOS instead of THOX, the ratio of BSG etch rate / TEOS etch rate and/or the ratio of BPSG etch rate / TEOS etch rate at 25°C is/are 5 or higher, preferably 10 or higher, more preferably 50 or higher, particularly 100 or higher.

[0008] The etch rate of the etching solution of the invention can be calculated as the difference in thickness of a film (BSG; BPSG; THOX; TEOS and like USG, etc.) before and after etching divided by etch time.

[0009] The water content is not higher than 70% by weight, preferably not higher than 30% by weight, more preferably about 30-5% by weight. The relative dielectric constant of the etching solution expresses an arithmetic mean of the relative dielectric constants of the components of the etching solutions other than the HF and inorganic acid.

[0010] Preferable examples of the inorganic acid include inorganic acids having a pKa value at 25°C of 2 or lower, for example, hydrochloric acid (pKa=-8), nitric acid (pKa=-1.8), hydrobromic acid (pKa=-9), hydroiodic acid (pKa=-10) and perchloric acid (a pKa-unmeasurably strong acid).

[0011] Examples of the organic acid include acetic acid (relative dielectric constant: 6.15 (20°C)), propionic acid (relative dielectric constant: 3.4 (40°C)), butyric acid (relative dielectric constant: 2.97(20°C)), isobutyric acid (relative dielectric constant: 2.63(71°C)), caprylic acid (relative dielectric constant: 2.63(71°C)), caprylic acid (relative dielectric constant: 2.63(71°C)), dichloroacetic acid (relative dielectric constant: 21 (20°C)), dichloroacetic acid (relative dielectric constant: 4.6 (60°C)), monofluoroacetic acid, difluoroacetic acid, trifluoroacetic acid, α -chlorobutyric acid, β -chlorobutyric acid, γ -chlorobutyric acid, lactic acid (relative dielectric constant: 22(70°C)), glycolic acid, pyruvic acid, glyoxalic acid, acrylic acid and like monocarboxylic acids, methanesulfonic acid, toluenesulfonic acid and like sulfonic acids, oxalic acid, succinic acid, adipic acid, tartaric acid, citric acid and like polycarboxylic acids.

[0012] Examples of the organic solvent having a hetero atom include methanol (relative dielectric constant: 32.6 (25°C)), ethanol (relative dielectric constant: 24.6 (25°C)), isopropanol (IPA, relative dielectric constant: 19.9 (25°C)), 1-propanol (relative dielectric constant: 22.2 (25°C)), 1-butanol (relative dielectric constant: 17.1 (25°C)), 2-butanol (relative dielectric constant: 15.5 (19°C)), t-butanol (relative dielectric constant: 11.4 (19°C)), 2-methyl-1-propanol (relative dielectric constant: 17.95 (20°C)), 1-pentanol (relative dielectric constant: 13.9 (25°C)), 1-hexanol (relative dielectric constant: 13.3 (25°C)), 1-heptanol, 4-heptanol, 1-octanol (relative dielectric constant: 10.34 (20°C)), 1-nonyla-Icohol, 1-decanol, 1-dodecanol and like alcohols; ethylene glycol (relative dielectric constant: 37.7 (20°C)), 1,2-propanediol (relative dielectric constant: 32.0 (20°C)), 2,3-butanediol, glycerin (relative dielectric constant: 42.5 (25°C)) and like polyols, acetone (relative dielectric constant: 20.7 (25°C)), acetylacetone, methyl ethyl ketone (relative dielectric constant: 18.51 (20°C)) and like ketones; acetonitrile (relative dielectric constant: 37.5 (20°C)), propionitrile (relative dielectric constant: 29.7 (20°C)), butyronitrile (relative dielectric constant: 20.3 (20°C)), isobutyronitrile (relative dielectric constant: 20.4 (20°C)), benzonitrile (relative dielectric constant: 25.2 (25°C)) and like nitriles; formaldehyde, acetaldehyde, propionaldehyde and like aldehydes; ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and like alkylene glycol mono alkyl ethers; tetrahydrofuran (relative dielectric constant: 7.6 (25°C)), dioxane (relative dielectric constant: 2.2 (25°C)) and like ethers, trifluoroethanol, pentafluoropropanol, 2,2,3,3-tetrafluoro propanol and like fluorine alcohols, sulfolane (relative dielectric constant: 43.3 (20°C)), nitromethane (relative dielectric constant: 35.87 (30°C)) and the like.

[0013] The relative dielectric constant of water is 78.3 (25°C).

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[0014] The content of HF is about 0.01-50% by weight, preferably about 1-5% by weight.

[0015] The water content is not higher than 70% by weight, preferably not higher than 30% by weight, more preferably about 0-5% by weight.

[0016] The content of the inorganic acid is about 1-99% by weight, preferably about 30-70% by weight.

[0017] The content of the organic acid is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0018] The content of the organic solvent having a hetero atom is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0019] The content of at least one member selected from the group consisting of the inorganic acid, organic acid and organic solvent having a hetero atom is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0020] The inorganic acid has a pKa at 25°C of about 2 or lower, preferably about -5 or lower.

[0021] The relative dielectric constant of the organic acid and organic solvent having an hetero atom is preferably about 40 or lower, more preferably about 10 or lower.

[0022] As the HF is usually used dilute hydrofluoric acid (50 wt. % aqueous solution). However, when the HF does not contain water, 100% HF may be also used.

[0023] In case of HCl, HBr and HI, an anhydrous etching solution can be prepared by blowing these gases through the etching solution.

55 [0024] Preferable etching solutions of the present invention and their compositions are shown below.

- + HF: IPA : water = 1-10% by weight : 70-99% by weight : 0-30% by weight
- HF: acetic acid: water = 0.5-5% by weight: 70-99.5% by weight: 0-30% by weight

- HF: HCI: water = 0.01-5% by weight: 1-36% by weight: 50-99% by weight
- HF: nitric acid: water = 0.01-5% by weight: 1-70% by weight: 20-99% by weight
- HF: acetone: water = 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: THF: water = 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: methanol: water = 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: ethanol: water = 1-10% by weight: 70-99% by weight: 0-30% by weight

[0025] The etching solution of the invention can be suitably used for selectively etching a doped oxide film of an article to be etched comprising an oxide film (BSG, BPSG, etc.) doped with B, P and the like and an undoped oxide film such as THOX, TEOS and like.

[0026] In the etching method of the present invention, the temperature of the etching solution is about 15-40°C.

[0027] Examples of the article to be etched include single crystalline silicon wafers, gallium-arsenic wafers and like wafers, especially the articles comprising a doped oxide film (BSG, BPSG, etc.) and an undoped oxide film (THOX, TEOS and like USGs).

[0028] The BSG etch rate of the etching solution of the invention is usually about 10-2000 nm/min, preferably about 40-500 nm/min.

[0029] The present invention can provide an etching solution which can selectively etch films doped with impurities, such as BSG, BPSG and the like, relative to THOX, TEOS and like USG, a method for producing an etched article using the etching solution and an etched article.

BEST MODE FOR CARRYING OUT THE INVENTION

[0030] The present invention will be explained in more detail with referring to Examples and Comparative Examples below.

Examples 1-2 and Comparative Examples 1-4 (inorganic acid)

[0031] Etching solutions were prepared by mixing HF, water, an organic solvent having a hetero atom (isopropyl alcohol (IPA), THF, acetone, methanol, ethanol), an organic acid (acetic acid) and inorganic acid (HCI, HNO₃) in the ratios shown in Table 1. Test substrates were produced by forming each of a thermal oxide (THOX) film, USG (TEOS) film, boron silicate glass (BSG) film and boron phosphosilicate glass (BPSG) film on a silicon substrate by CVD method using a tetraethoxysilane gas. The etch rate and etch selectivity of the etching solutions on the test substrates were determined.

[0032] In addition, the etch rate and selectivity of conventional HF-H₂O and HF-NH₄F-H₂O etching solutions were determined in the above-mentioned manner as Comparative Examples.

[0033] The etch rate was determined by measuring the thickness of the films before and after etching with an Auto EL-III ellipsometer manufactured by Rudolf Research.

[0034] The etch rates of the etching solutions were calculated as the difference in thickness of films before and after being etched at 25°C divided by etch time.

[0035] The results of the etching solutions with each composition are shown in Table 1 to Table 8.

[0036] The relative dielectric constant is that of a solvent (an organic solvent having a hetero atom or an organic acid) + water at 25°C, expressed as a calculated value of an average of the relative dielectric constants of the solvent and water having the particular composition.

[0037] Average of relative dielectric constants = [78.3 x (percentage by weight of water) + (relative dielectric constant of solvent at 25°C) x (percentage by weight of solvent)] / [(percentage by weight of water) + (percentage by weight of solvent)]

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etchant
(PA)
alcohol
HF-H ₂ O-isopropyl

_							_		_							_				_
BPSG	/TEO	s	sele	ctiv	ity	'	30	15	12	9.8	ı	1	•	,	,		. 1		1	
BSG/	TEOS	sele	ctiv	ity	r		34	12	8.5	7.3	40	27	19	10	4.1		3.9		4.0	
BPSG	/THO	×	sele	ctiv	ity		28	21	17	14	1	,	,	,	,		1		,	
BSG/	THOX	sele	ctiv	ity			31	17	12	10	09	37	28	15	6.5		6.3		9.9	
SSGE	etch	rate	(A/m	in.)			330	1160	1650	1950	1	1	ı	1	-		ı		ı	
BSG	etch	rate	(A/min	•			370	920	1190	1450	120	2200	6500	12000	380		750		1980	
TEOS	etch	rate	(A/m	in.)			11	9/	140	200	ო	82	230	1200	63		190		490	
THOX	etch	rate	(A/m	in.)		·	12	55	97	140	7	59	350	820	85		120		300	
Relative	dielectric	constant of	solvent	(IPA)+water	(calculated	value)	23.0	35.3	47.6	59.9	21.7	26.4	30.2	34.5	•		ı		•	
Solvent	(IPA)	-uaouoo	tration	æ)			06	70	20	30	94	80	70	60	0		0		0	
Water	-uoɔ	cen-	tra-	tion	(8)		S	25	45	65	ო	10	15	20	66		86		95	
HF	-uoo	cen-	tra-	tion	(8)		2	S.	S	S	m	10	15	20	1		7		m	
Relative	dielectric	constant of	solvent				19.9	19.9	19.9	19.9	19.9	19.9	19.9	19.9	(78.3)		(78.3)		(78.3)	
Sol-	vent						IPA	(Water	~	(Water	~	(Water	_							
							Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Comp.	Ex. 1	Comp.	Ex. 2	Comp.	Ex. 3

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HF-H20-acetic acid etchant

	Solvent	Relativ	HF con-	Water	Solvent	Relative	THOX	TEOS	BSG	BPSG	BSG/T	BPSG/	BSG/T	BPSG/
		ø	centra-	concen-	(acetic	dielectric	etch	etch	etch	etch	НОХ	THOX	EOS	TEOS
		dielect	tion (%)	tration	acid) con-	constant	rate	rate	rate	rate	selec	selec	selec	selec
		ric		æ)	centration	of solvent	(A/mi	(A/mi	(A/mi	(A/mi	tivit	tivit	tivit	tivit
		constan			(%)	(acetic	n.)	<u></u>	<u>.</u>	n.)	>	^	>	>
		t of		,		acid)+					;			
		solvent				water								
						(calculat-						•		
Ex. 9	Acetic	6.15	1	1	86	6,88	10	14	530	750	. 53	75	38	54
Ex. 10	Acetic	6.15	1.25	1.25	97.5	7.06	12	18	1200	940	100	78	67	52
	acid					•								
Ex. 11	Acetic	6.15	1.5	1.5	. 76	7.25	17	22	1600	1300	94	92	73	59
Ex. 12	Acetic	6.15	2	2	96	7.62	25	33	2600	•	100	J	79	ı
	acid	,	,	,		ı								
Ex. 13	Acetic	6.15	2.5	2.5	95	80	35	45	3600	1	110		80	ı
	acid	,	,	r	Š	ć	9	L	60,		,		;	
Ex. 14	Acetic	GT.0		ກຸ	94	8.38	,	c c	4 600		170	1	84	,
Ex. 15	Acetic	6.15	'n	ß	06	9.95	97	140	8900	•	92	,	64	,
	acid													
Ex. 16	Acetic	6.15	1.25	S.	93.75	9.80	18	23	1600	ı	68	ı	70	1
	acid	,	(,	i c	i (Ġ	(•			;	
Ex. 1/	Acetic	6.13	1.25	01	64.75	13.5	2	35	1300	1	69	ı	4	1
85	Acetic	35	1.25	20	78.75	20.8	32	46	970	ı	30	,	[2	ı
	acid) 	1	}))					†	
Ex. 19	Acetic	6.15	1.25	30	68.75	28.1	39	28	830	1	21	ı	14	1
	acid				,			•						
Ex. 20	Acetic	6.15	1.25	40	58.75	35.4	9	65	019	ı	. 17	ı	10	1
	acid	3,	30.	0	36 97	7	Ş	,	ú				•	
EX. 61	Acerac	CT:0	67.1	200	7.0	45.1	<u>د</u> ن	7	020	•		ı	7.9	ı
	acta								,					

HF-H2O-tetrahydrofurane (THF) etchant

Relative	HE	Water	Sol-	Relative	THOX	TEOS	BSG	BPSG	BSG/	BPSG	BSG/	BPSG
lielectric		-uoo	vent	dielectric		etch	etch	etch	THOX	/THO	TEOS	/TEO
constant		cen-	(THE)	constant of		rate	rate	rate	sele	×	sele	S
of solvent	tra-	tra-	-uoo	solvent		(A/m	(A/m	(A/m	ctiv	sele	ctiv	sele
	tion	tion	cen-	(THF) +water		in.)	in.)	in.)	ity	ctiv	ity	ctiv
	(%)	(%)	tra-	(calculated		ı	•			ity		ity
			tion	value)								
			(%)									
7.6	5	5	90	11.3	3	4	510	330	170	110	130	83
7.6	ഹ	22	70	26.2	31	42	069	830	22	.27	16	50
7.6	'n	45	20	41.1	64	85	890	1200	14	19	10	14
7	ĸ	5.5	9	56.0	110	150	1200	1600	-	٦.	<u>«</u>	=
	Relative dielectric constant of solvent 7.6 7.6 7.6	Relative HF dielectric conconstant centric ce	HF We con- control tra- train train tra- train tra	Relative HF lielectric conconstant cention of solvent tration (%) 7.6 5 7.6 5	Relative HF Water Solution idelectric con- con- vent constant cen- (THF) of solvent tra- con- tion tion cen- (%) (%) tra- 7.6 5 5 90 7.6 5 45 50 7.6 5 45 50 7.6 5 45 50 7.6 5 65 30 7.6 5 65 30 7.6 5 65 30	Relative HF Water Sol- iielectric con- con- vent constant cen- (THF) of solvent tra- con- tion tion cen- (%) (%) tra- 7.6 5 5 90 7.6 5 45 50 7.6 5 45 50 7.6 5 65 30 7.6 5 65 30 7.6 5 65 30	Relative HF Water Sol- Relative THOX T itelectric con- con- vent dielectric etch etch constant cen- (THF) constant of rate rate rate solvent tra- cen- (THF) +water in.) in. in. (%) (%) tra- (calculated in.) in. in. 7.6 5 5 90 11.3 3 7.6 5 45 50 41.1 64 7.6 5 5 30 41.1 64 7.6 5 5 30 56.0 110	Relative HF Water Sol- Relative THOX TEOS idelectric con- con- vent dielectric etch etch constant cen- (THF) constant of rate rate solvent tra- con- solvent (A/m (A/m tion tion cen- (THF)+water in.) in.) (%) tra- (calculated in.) in.) tion value) (%) tion value) 7.6 5 5 90 11.3 3 4 7.6 5 45 70 26.2 31 42 7.6 5 5 70 56.0 110 150	Relative HF Water Sol- Relative THOX TEOS BSG idelectric con- con- vent dielectric etch etch etch constant cen- (THF) constant of rate rate rate solvent tra- con- solvent (A/m (A/m tion tion cen- (THF) + water in.) in.) tion tra- (calculated in.) in.) in.) 7.6 5 5 90 11.3 3 4 510 7.6 5 45 50 41.1 64 85 890 7.6 5 5 70 56.0 110 150 1200	Relative HF Water Sol- Relative THOX TEOS BSG BFSG BFSG	Relative HF Water Sol- Relative THOX TEOS BSG BFSG BSG/BSG/BSG/BSG/BSG/BSG/BSG/BSG/BSG/BSG/	Relative HF Water Sol- Relative THOX TEOS BSG BPSG BSG/ idelectric con- con- vent dielectric etch etch etch rate THOX constant cen- (THF) constant of rate rate rate rate sele solvent tra- con- (THF) +water in.) in.) in.) in.) ity (%) tra- (THF) +water in.) in.) in.) ity ity 7.6 5 5 90 11.3 3 4 510 330 170 7.6 5 45 50 41.1 64 85 890 1200 14 7.6 5 5 30 41.1 64 85 890 1200 14 7.6 5 5 30 41.1 64 85 890 1200 11

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HF-H20-acetone etchant

Relative	HE	Water	-tos	Relative	THOX	TEOS	BSG	BPSG	BSG/	BPSG	/SSE	BPSG
	-uoo	-uoo	vent	dielectric	etch	etch	etch	etch	THOX	/THO	TEOS	/TEO
	cen-	cen-	(aceto	constant of	rate	rate	rate	rate	sele	×	sele	ß
	tra-	tra-	ne)	solvent	(A/m	(A/m	(A/m	(A/m	ctiv	sele	ctiv	sele
	tion	tion	-uoo	(acetone)+	in.)	in.)	in.)	in.)	ity	ctiv	ity	ctiv
	(%)	(%)	-uəɔ	water (cal-						ity		ity
			tra-	culated								
			tion	value)								
			(8)									
]	2	S	06	23.7	3	4	410	250	140	83	100	63
	2	25	70	35.9	24	53	440	520	18	22	15	18
	S	45	20	48.0	49	. 67	620	260	13	16	9.3	11
	LC.	65	30	60.1	96	140	960	1300	10	14	6.9	6.9

HF-H2O-methanol etchant

	_		<u></u>	_	_	_	\neg		_		_
_	/TEO	-			ity			10	26	,	<i>-</i>
BSG/	TEOS	sele	ctiv	ity				6.3	19	ţ	_
BPSG	/THO	×	sele	ctiv	ity			150		_	
BSG/	THOX	sele	ctiv	ity	·			88	57		~
BPSG	etch	rate	(A/m	in.)				73	230		=
BSG	etch	rate	(A/m	in.)				44	170		
TEOS	etch	rate	(A/m	in.)				7	σ	• :	43
THOX	etch	rate	(A/m	in.)				0.5	•	· ;	c
Relative	(metha- dielectric	constant of	solvent	(metha-	nol)+water	O	value)	34.0	35.0	•	
Solvent	(metha-	nol)	concen-	tration	(8)			94	G	?	~
Water	-uoo	cen-	tra-	tion	(&)			3	u	,	•
HE	-uoo	cen-	tra-	tion	%			<u>س</u>	u	ר	•
Relative	dielectric	constant	of solvent					32.6		32.0	1
Solvent) ; ; ;							Ev 30 Methanol	ווככוומווסד	Ex. 31 Methanol	
								30		٦٢ ·	
					:			6	4 1	ĭ	

HF-H2O-ethanol etchant

3 7 A	ity ity 23	28	7 9 250 210 36 30	36	210	250	6	7	water (calculated value)	·		cen- tra- tion (%)	(%) cen- tra- tion (%)	(%) (%) central transition (%) (%) (%) (%) (%)	(%) (%) centraction (%) (%) (%)
لد	<u> </u>	1	ity						water (ca)culated	cen-	(%)	<u>.</u>	*	*)	8)
ΙV	ctiv	ity	ctiv	ity	in.)	in.)	in.)	in.)	Toriginal .	_con_	tion	tion	ţį	ti	ti
]e	sele	ctiv	sele	ctiv	(A/m	(A/m	(A/m	(A/m	(ethanol)	anol)	tra-	ı,			
လ		sele	×	sele	rate	rate	rate	rate	constant of	(eth-	cen-		cen-	constant cen-	
င္မ	<u>-</u>	TEOS /TEO	/THO	THOX	etch	etch	etch	etch	dielectric etch etch etch THOX /THO TEOS /	vent	con-		con-		
SG	BP	BSG/	BPSG	BSG/	BPSG	BSG	TEOS	XOHL	Relative THOX TEOS BSG BPSG BSG/ BPSG BSG/ BPSG	Sol-	Water		HF	Ξ	Ξ

 ${\rm HF-NH_4F-H_2O}$ etchant (Comparative Examples)

									_				,		
BPSG	/TEO	တ	sele	ctiv	ity			1	1	1	1	1	ı	1	
/9SB	TEOS	sele	ctiv	ity	:			0.5	1.3	7.0	0.5	0.4	0.4	0.4	
BPSG	/THO	×	sele	ctiv	ity			1	1	ţ	ı	1	1	ı	
BSG/	THOX	sele	ctiv	ity				9.0	2.2	1.4	6.0	9.0	9.0	7.0	
BPSG	etch	rate	(A/m	in.)	,			1	ţ	_	1	1	1	ı	
BSG	etch	rate	(A/m	in.)	:			110	620	440	350	270	230	200	
TEOS	etch	rate	(A/m	in.)				230	480	640	700	720	019	450	
THOX	etch	rate	(A/m	in.)				170	280	320	400	420	390	300	
Sol-	vent	(water	con-	cen-	tra-	tion	(8)	59.9	96	93	88	78	89	59.3	
NH4F	con-	Gen-	tra-	tion	(%)			39.1	2	5	10	20	30	38.7	
	-	Ī		tion	. (8)				2	2	2	2	2	2	
Relative	dielectric	constant	of solvent		,			(78.3)	(78.3)	(78.3)	(78.3)	(78.3)	(78.3)	(78.3)	
Solvent								(Water)	(Water)			(Water)	(Water)	(Water)	
								Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex.	10

HF-H2O-acid-added etchant

I											1			;				
BSG/	TEOS	sele	ctiv	ity	: -	14	13	13	14	12	16	5.9		ഹ				
BPSG	/THO	×	sele	ctiv	ity	1	1	1	t	ı	1	1		1			• • • • •	
BSG/	THOX	sele	ctiv	ity		26	23	21	24	19	22	8.7		7.1				
BPSG	etch	rate	(A/m	in.)	:	1	١	ı	1	١	ì	1	-					
BSG	etch	rate	(A/m	in.)		440	1200	2500	4300	4500	5300	850						
TEOS	etch	rate	(A/m	in.)		32	68	200.	300	380	340	170						
THOX	etch	rate	(A/m	in.)		17	53	120	180	240	240	120						
Acid	concen	tratio	(%) u			35.9	35.8	35.6	35.5	35.3	68.6	83.3						
Water	-uoɔ	cen-	tra-	tion	(8)	64	63.9	63.9	63.8	63.7	30.4	15.7						
HF	-uop	cen-	tra-	tion	(%)	0.1	0.25	0.5	0.75	н	F							
pKa of	acid				:	8-	8-	8-	8-	81	-1.8	2.15		(pKa1)	7.20	(pKa2)	12.4	(6.43.4)
Added	acid		_			HC1	HCI	НСТ	HC1	HC1	HN03	H3P04						
						Ex. 34	Ex. 35	Ex. 36	Ex. 37	Ex. 38	Ex. 39	Comp. Ex.	11					

Claims

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- 1. An etching solution comprising hydrofluoric acid, wherein a ratio of an etch rate of a boron silicate glass film (BSG) or boron phosphosilicate glass / an etch rate of a thermal oxide film (THOX) at 25°C is 10 or higher.
- 2. The etching solution according to claim 1, wherein a solvent in the etching solution has a relative dielectric constant of 61 or lower.
- 3. The etching solution according to claim 1, the solution containing at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.
 - 4. The etching solution according to claim 1, the solution containing (i) water and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 70% by weight or lower.
 - 5. The etching solution according to claim 1, wherein the weight ratio of HF: isopropyl alcohol: water is 0.1-50% by weight: 30-99% by weight: 0-70% by weight.
- 6. The etching solution according to claim 1, wherein the weight ratio of HF: acetic acid: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
 - 7. The etching solution according to claim 1, wherein the weight ratio of HF: tetrahydrofuran: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
- 25 **8.** The etching solution according to claim 1, wherein the weight ratio of HF : acetone : water is 0.1-50% by weight : 30-99.9% by weight : 0-70% by weight.
 - 9. The etching solution according to claim 1, wherein the weight ratio of HF: methanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
 - **10.** The etching solution according to claim 1, wherein the weight ratio of HF: ethanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
 - 11. The etching solution according to claim 1, the solution comprising an inorganic acid.
 - 12. The etching solution according to claim 11, wherein the inorganic acid has a pKa value at 25°C of 2 or lower.
 - **13.** The etching solution according to claim 11, wherein the weight ratio of HF: HCI: water is 0.01-50% by weight: 1-36% by weight: 0-99% by weight.
 - **14.** The etching solution according to claim 11, wherein the weight ratio of HF: HNO₃: water is 0.01-50% by weight: 1-70% by weight: 0-99% by weight.
- **15.** A method for producing an etched article by etching an article to be etched with the etching solution as defined in any of claims 1-14.
 - **16.** An etched article which is obtainable by the method of claim 15.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/06502

							
	IFICATION OF SUBJECT MATTER C1 ⁷ H01L 21/306, 21/308, C1 ⁷ C09K 13/08						
According to	o International Patent Classification (IPC) or to both nat	tional classification and IPC					
B. FIELDS	SEARCHED						
Int.							
Jits Koka	ion searched other than minimum documentation to the uyo Shinan Koho 1926-1996 i Jitsuyo Shinan Koho 1971-2000	Jitsuyo Shinan Toroku K Toroku Jitsuyo Shinan K	oho 1996-2000 oho 1994-2000				
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"A" docum conside "E" earlier date "L" docum cited to special "O" docum means "P" docum than th	I categories of cited documents: ent defining the general state of the art which is not tred to be of particular relevance document but published on or after the international filing ent which may throw doubts on priority claim(s) or which is o establish the publication date of another citation or other I reason (as specified) ent referring to an oral disclosure, use, exhibition or other tent published prior to the international filing date but later te priority date claimed	"T" later document published after the interpriority date and not in conflict with the understand the principle or theory und document of particular relevance; the considered novel or cannot be considered to involve an inventive ste combinated with one or more other such combination being obvious to a perso document member of the same patent	he application but cited to lerlying the invention cannot be cred to involve an inventive e claimed invention cannot be p when the document is h documents, such in skilled in the art family				
09 I	actual completion of the international search February, 2000 (09.02.00)	Date of mailing of the international sea 22 February, 2000 (
	nailing address of the ISA/	Authorized officer					
Facsimile N		Telephone No.					

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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT			
ategory*	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No
{	Claims (Family: none)		
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